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Chemistry of the 1,2-Dioxetane Ring System.

Chemiluminescence, Fragmentations, and Catalyzed Rearrangements.

by

Keith A. Horn, Ja-young Koo, Steven P. Schmidt,

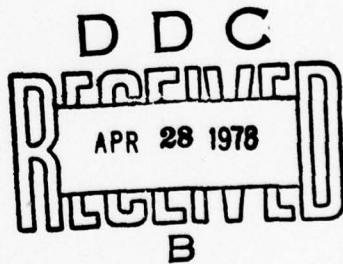
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CHEMISTRY OF THE 1,2-DIOXETANE RING SYSTEM.
CHEMILUMINESCENCE, FRAGMENTATIONS, AND CATALYZED REARRANGEMENTS.

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Introduction and Scope

The chemistry of the cyclic four-membered ring peroxides known as dioxetanes has recently come under heavy scrutiny mainly because of the intriguing chemiluminescence that thermolysis elicits from these compounds. The mechanism for the thermal conversion of a ground state dioxetane to an excited state product has been probed experimentally with substituent, isotope, solvent, temperature, and pressure effects. Theoretical calculations have been carried out at several levels of sophistication to determine the reaction coordinate. Many dioxetanes have been prepared to test the various theories proposed. Recently, several dioxetanes have been prepared that exhibit very high quantum efficiencies for chemiluminescence. The generation of excited states from these dioxetanes proceeds by a mechanism different from that of simple alkyl dioxetanes. This article will concentrate in large part on these aspects of dioxetane chemistry. Also discussed will be the reactions of dioxetanes with several reagents. Finally, dioxetanes have been used as a tool to probe the pathway for various excited state processes. In these studies advantage was taken of the non-photochemical source of electronically excited states. We will briefly review the

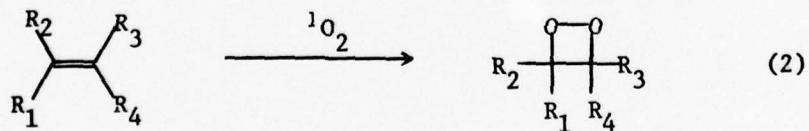
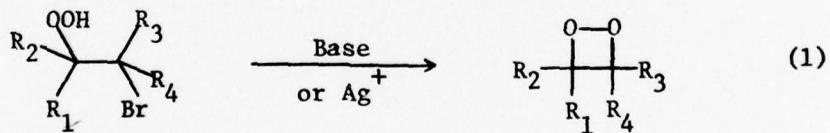
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recent results from these investigations.

In order to keep this article to a manageable length, we have restricted our coverage to the most significant reports published in the period from January 1975 to December 1977. Much of the chemistry of dioxetanes that appeared prior to this period has been critically reviewed by Wilson¹ and by Adam.² The interested reader is referred to these earlier excellent reviews as well as the original literature for a description of experimental techniques and for an historical perspective on the chemistry of 1,2-dioxetanes.

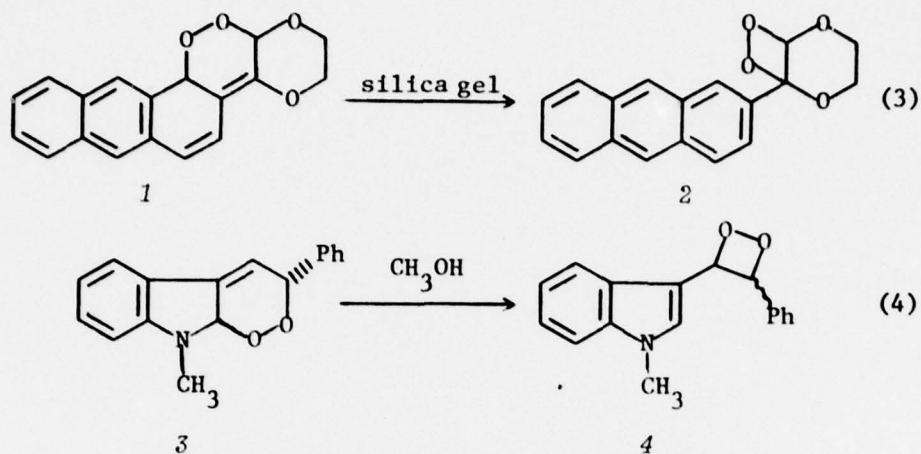
Synthesis and Structure of 1,2-Dioxetanes

There are at present two general methods available for the preparation of 1,2-dioxetanes. Historically, the first well characterized dioxetane was synthesized by the dehydrohalogenation of 2-methyl-2-hydroperoxy-3-bromobutane with base.³ Eliminative cycloadditions based upon this example (equation 1) have been developed and used to prepare dioxetanes of diverse structure. The second general procedure for the preparation of 1,2-dioxetanes centers on the formal 2+2 cycloaddition of singlet oxygen to various olefins (equation 2).⁴ Practically, this approach is limited to cases in which the olefin is relatively electron rich and does not contain abstractable allylic hydrogen atoms. The advantage of the photooxidation, of course, is the extremely mild conditions under



which it can be carried out. Recently Schaap and coworkers⁵ have reported the preparation of dioxetane 2 by the silica gel catalyzed rearrangement of endoperoxide 1. Similarly, Matsumoto and Kondo⁶ suggest that the unisolated dioxetane 4 is a result of the rear-

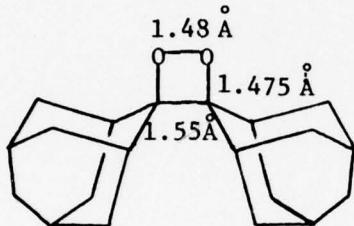
rangement of 3 in the presence of alcohols. While this synthetic approach probably will not have general utility, it does provide another avenue for the preparation of 1,2-dioxetanes.



It is not our purpose in this article to provide a detailed analysis of the preparation of dioxetanes. The interested reader should, of course, consult the original articles. However, we have compiled in Table 1 those 1,2-dioxetanes that have been prepared during the period of this review and have indicated the method of their preparation and certain of their characteristics. The variety of substituted dioxetanes that have been prepared recently is quite impressive and testifies to the general utility of the procedures available for preparation of this ring system. Several chemiluminescent reactions have been postulated to proceed through unisolated 1,2-dioxetanes. In general, the major evidence for the intermediacy of a dioxetane includes finding the appropriate cleavage products and light emission. Though these suspected dioxetanes are not included among those in Table 1, they will be discussed in a subsequent section.

The ground state structure of 1,2-dioxetanes has been suggested to be important in determining the stability of the ring system and to some extent in defining their chemiluminescent behavior. The structure of the unusually stable dispiro(adamantane-2,3'-[1,2]dioxetane-4',2"-adamantane) (5) has been determined using X-ray

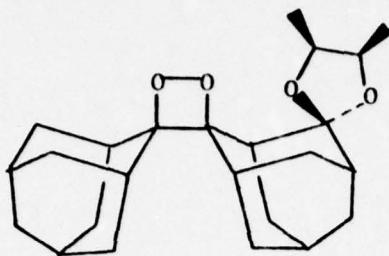
crystallography by Wynberg and coworkers.⁷ This study showed that the length of the O-O bond is 1.48 Å, about equal to that in hydrogen peroxide. The C-O bond is 1.475 Å, a relatively long bond, while the dioxetane ring C-C bond is approximately as expected with a length of 1.549 Å. Interestingly, the four-membered ring is non-planar, one oxygen atom being lifted ca. 20° from the plane defined by the two carbons and the remaining oxygen of the four-membered ring. The ground state structure of this molecule may offer some insight into the reasons for its extraordinary stability. Stretching of the O-O bond causes a compression of the adamantyl substituents. The alternative twisting motion does not appear to be sterically restricted.



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The electronic structure of tetramethyldioxetane was investigated using photoelectron spectroscopy by Brown.⁸ This study showed that the photoelectron spectrum of the dioxetane is similar to that of other cyclic peroxides. The first band in the spectrum shows a vertical ionization potential of 8.98 eV and is assigned to removal of an electron from an antisymmetric π^* orbital.

An interesting structural modification of dioxetane 5 has permitted Wynberg and coworkers to prepare an optically active 1,2-dioxetane (6) by photooxidation of the corresponding resolved olefin. When this dioxetane was thermolyzed at 197° in dodecane, chemiluminescence was detected.⁹ These workers successfully detected circular polarization of the emitted light. This is the first example of this phenomenon, and the authors raise the interesting possibility that many bioluminescent reactions also generate circularly polarized light.



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Mechanisms for Chemiluminescence of 1,2-Dioxetanes

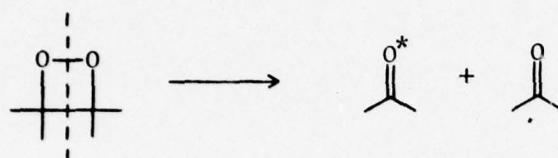
The chemical transformations of 1,2-dioxetanes that result in excited state generation have been the center of active and increasing investigation over the past few years. Some clear patterns are now beginning to emerge and, as is often the case, the situation is somewhat more complicated than originally presumed.

Historically, the first dioxetanes prepared contained simple alkyl or alkoxy substituents. These dioxetanes have several features in common. The activation energy for their decomposition ranged from 20-30 kcal/mol depending upon steric and ring strain factors. The yield of electronically excited carbonyl-containing products centered in the range from 10-30% and, most interestingly, the yield of directly formed excited triplet carbonyl compound was typically more than fifty times the yield of directly formed excited singlet state.¹⁰ This reactivity pattern, in particular the large triplet to singlet ratio, gave rise to two postulated mechanisms for chemical light generation by these dioxetanes. The first, originally considered by McCapra^{11a} and Kearns,^{11b} postulates simultaneous cleavage of both the O-O and the C-C bonds of the dioxetane in a concerted manner to directly generate electronically excited products. Later Turro¹² expanded this picture by suggesting that a spin multiplicity change occurred coincidentally with bond cleavage, thereby rationalizing the high triplet to singlet excited state ratio. The second general mechanistic scheme was advanced by Richardson.¹³ This approach favors a stepwise reaction passing through the intermediate 1,4-biradical formed by cleavage of the

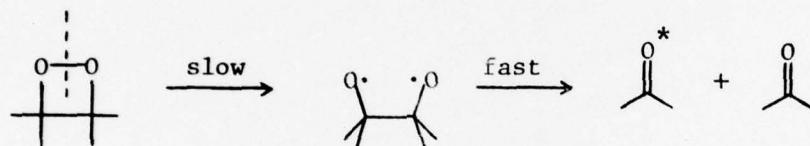
strained O-O bond of the four-membered ring peroxide. The intermediate thus formed is then postulated to partition between excited state carbonyl products of both singlet and triplet multiplicity and ground state carbonyl products. These paths are represented in Scheme 1. During the period covered in this review, several critical experiments have been performed in an attempt to distinguish between these two paths.

Scheme 1

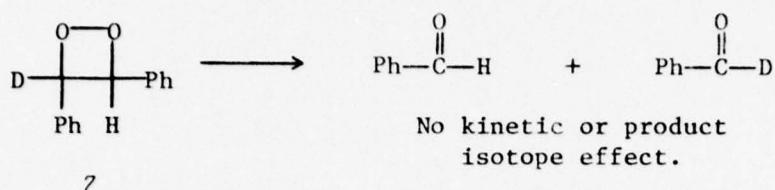
Concerted



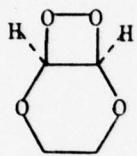
Stepwise



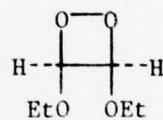
Koo and Schuster¹⁴ investigated the effect of deuterium substitution on the rate of reaction, the yield of excited states, and the regiospecificity of excited state generation for *trans*-3,4-diphenyl-1,2-dioxetane (?). The key postulate in this work is that a change in hybridization at the carbon atoms of a dioxetane during the rate determining step should cause a measurable α -secondary deuterium isotope effect. In the biradical mechanism the hybridization at carbon of course does not change during the O-O bond cleavage step; in the concerted mechanism the hybridization changes from sp^3 toward sp^2 as the reaction approaches the transition state. This hybridization change gives rise to the prediction of an inverse deuterium isotope effect. In fact, no isotope effect whatsoever was observed. These results were taken as consistent only with the biradical mechanism.



In another study, Wilson¹⁵ and coworkers prepared and studied a series of alkoxy substituted dioxetanes. The activation parameters for dioxetanes *8* and *9* were nearly identical at *ca.* 24.5 kcal/mol. This observation was taken to indicate that the 3-4 kcal/mol of ring strain incorporated in bicyclic dioxetane *8* is not



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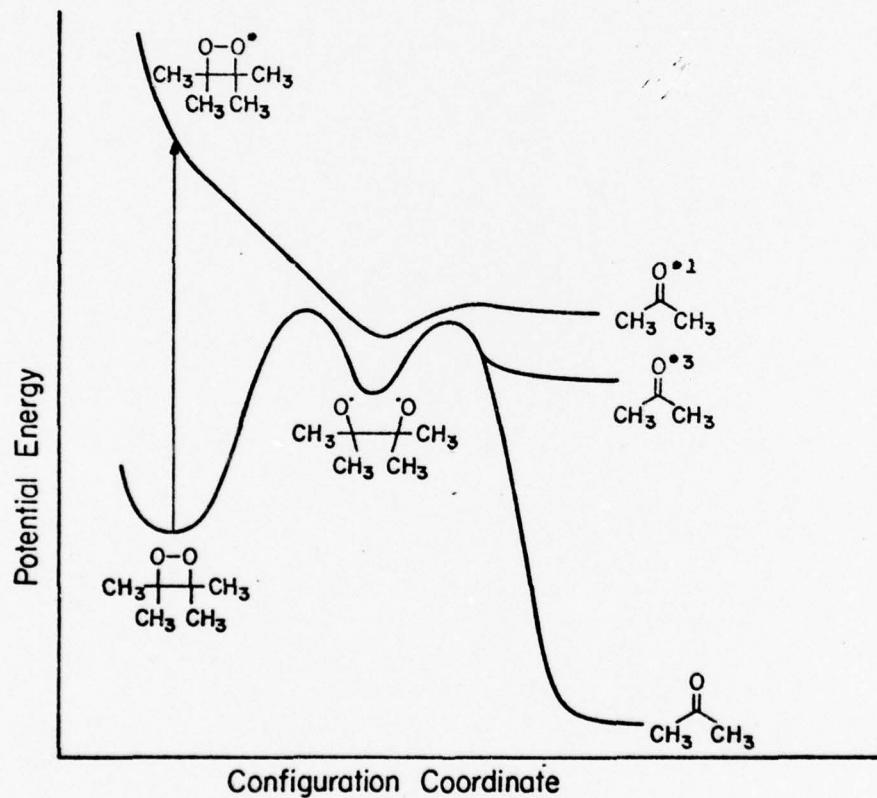
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released until after the transition state is reached. The implication of this conclusion is that the C-C bond of the dioxetane is not significantly lengthened in the transition state and that the biradical path best describes the reaction coordinate.

Simo and Stauff¹⁶ investigated the influence of triplet quenchers and radical scavengers on the intensity and the decay kinetics of the chemiluminescence from thermolysis of trimethyldioxetane. These workers found that the Stern-Volmer constants for the quenching of chemiluminescence by tri-*t*-butylphenol is about six times larger than that for 1,3-pentadiene under similar conditions. Since 1,3-pentadiene already quenches triplet acetone with a diffusion limited rate, they suggest that these findings mean that the phenol must be intercepting a relatively long-lived precursor to the electronically excited state. Another possible explanation, however, is that the phenol is acting as an acid causing the rapid dark path reaction of the dioxetane and hence giving rise to an apparent large Stern-Volmer slope. The interesting results reported

in this work certainly warrant further attention.

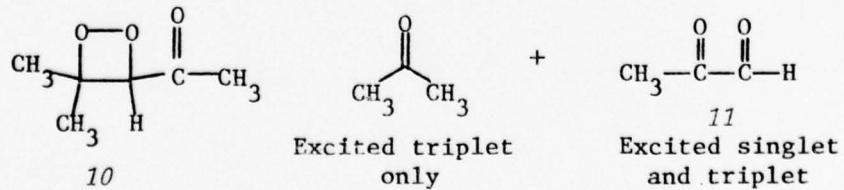
In an investigation employing picosecond spectroscopy Kaulmann, Schuster and coworkers¹⁷ probed the excited state surface for tetramethyldioxetane. They found that excited singlet acetone appeared within 10 psec of excitation by a 264 nm pulse generated from a mode-locked neodymium phosphate laser. This observation was coupled with the finding that the yield of singlet acetone from photolysis of tetramethyldioxetane is wavelength dependent (being higher at shorter wavelength) to suggest a consistent reaction path, shown in Figure 1. In this mechanism, excitation leads to an excited state of the dioxetane which has at least two exit channels. The first



channel generates singlet excited acetone by rapid simultaneous cleavage of both the O-O and the C-C bonds. The second channel is a vibrational cascade in which excess energy is transferred to the medium or at least to non-reactive vibrational modes. Eventually this relaxation process leads to cleavage of the O-O bond and generation of the same biradical intermediate obtained from thermolysis of the dioxetane. The biradical, in a subsequent step, then partitions between triplet and singlet excited acetone and acetone ground state. This interpretation is consistent with the energy surfaces calculated by Goddard and Harding¹⁸ (see below). Also, this reaction path is consistent with simple spin conservation notions.

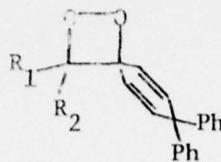
In another study of tetramethyldioxetane, Kelm and coworkers¹⁹ investigated the pressure dependence of the indirect chemiluminescence with 9,10-dibromoanthracene in a variety of solvents. In the pressure range from 1 atm to *ca.* 1000 atm, they found activation volumes of 9 and 11 cm³/mol in toluene and chlorobenzene respectively at 60°. By comparison with other homolytic cleavage reactions, the authors conclude that these observations favor a concerted rearrangement. However, they add that the biradical is not necessarily excluded by the findings.

In a recent study Horn and Schuster²⁰ have investigated the properties of 3-acetyl-4,4-dimethyldioxetane (10). This compound represents the first example of a dioxetane substituted with a powerful electron withdrawing group and provides the opportunity to examine the partitioning of excitation energy among dissimilar carbonyl compounds. Interestingly, thermolysis of this dioxetane generates not only the excited singlet and triplet of methylglyoxal (11) (64 and 55 kcal/mol above ground state, respectively), but



also produces an easily detected quantity of triplet acetone ($E_T = 78$ kcal/mol). Moreover, the ratio of triplet to singlet excited methylglyoxal was determined to be 9 ± 3 for this compound. Significantly, the energies of both methylglyoxal excited states are well below the energy expected for the biradical intermediate. The relatively low triplet to singlet excitation ratio is best interpreted as a result of the nearly statistical partitioning of the suspected biradical intermediates among the available spin states of the low energy dicarbonyl compound. Another example of a nearly statistical triplet to singlet excited state ratio comes from thermolysis of the bis-adamantyl substituted dioxetane 5. Lechtken and coworkers²¹ have determined by differential scanning calorimetry that rearrangement of 5 to two adamantanones is exothermic by 75 kcal/mol. The activation energy for this reaction was determined by Schuster, Turro, and coworkers²² to be 34.6 kcal/mol. Simple addition²³ puts the transition state for this reaction nearly 110 kcal/mol above ground state products and at least 25 kcal/mol above singlet excited adamantanone. As in the case of acetyl dioxetane 10 the nearly equal exothermicity for formation of either triplet or singlet excited product leads to a nearly statistical yield. However, it should be pointed out that for a transoid biradical intermediate, the extra exothermicity of 5 caused by steric interactions of the adamantyl groups should be dissipated. And the relationship of the biradical to the excited products should be qualitatively similar to other alkyl substituted dioxetanes.

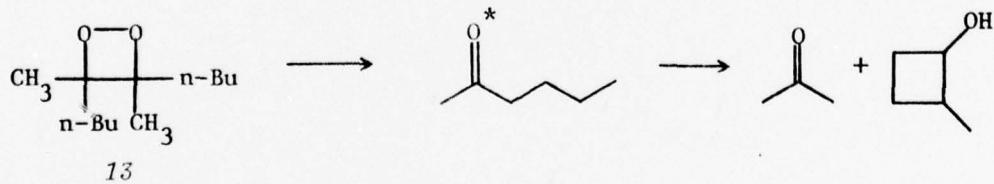
Zimmerman and coworkers²⁴ have prepared a series of dioxetanes substituted with a 1,4-cyclohexadiene ring (12). Of particular interest is the observation that these compounds fragment to generate the cyclohexadienone and a second carbonyl fragment. The portion of the dienone fragment that is formed in the excited state, of course, may go on to undergo the "Type A" photochemical rearrangement. The efficiency of formation of this rearrangement product varied only slightly (12-17%) as the nature of the substituents R_1 and R_2 was changed. Importantly, the excitation energies of the second fragments bracket that of the dienone triplet. To explain



14 a, $R_1 = Me, R_2 = Ph$
 b, $R_1 = Me, R_2 = m\text{-MeOPh}$
 c, $R_1 = Me, R_2 = 2\text{-Naph}$
 d, $R_1 = n\text{-Bu}, R_2 = Ph$

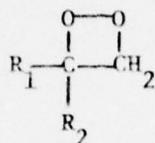
the constancy of the dienone excitation efficiency the authors suggested that there is a large kinetic factor favoring formation of $n\pi^*$ triplet states during dioxetane decompositions. However, as we shall see in a moment, at least for dioxetanes substituted with relatively easily oxidized groups, this is certainly not the case.

A point of apparent confusion regarding the yield of excited triplet and singlet states from the thermolysis of di-*n*-butyl-dimethyldioxetane (13) has been cleared up. Foote and Darling²⁵ reported that this compound fragmented thermally to yield 3.5% excited triplet and 5% excited singlet. This very low triplet to singlet ratio is most uncharacteristic of alkyl substituted dioxetanes. In a reinvestigation of this compound, Wilson and coworkers²⁶ report that they observe a triplet to singlet excitation ratio of about 300, more in line with other similar compounds.



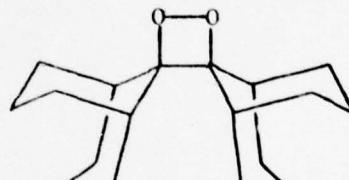
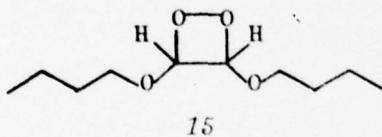
Richardson and his students²⁷ have presented the kinetic data and activation parameters for the thermolysis of dioxetanes 14a-d in methanol. This report again points out the powerful effect that impurities in methanol have on the rate of reaction of and the yield of light from dioxetanes. The authors report that increased phenyl

substitution has little effect on the rate of the thermolysis of the dioxetanes in EDTA treated methanol solvent. These results are used to support the stepwise decomposition mechanism in which the peroxide bond is cleaved in the rate determining step.



14 a, $\text{R}_1 = \text{R}_2 = \text{CH}_3$
 b, $\text{R}_1 = \text{CH}_3, \text{R}_2 = \text{C}_6\text{H}_5$
 c, $\text{R}_1 = \text{R}_2 = \text{C}_6\text{H}_5$
 d, $\text{R}_1 = \text{R}_2 = \text{C}_6\text{H}_5\text{CH}_2$

Lechtken²⁸ reports that when the thermolysis of tetramethyldioxetane, adamantyldioxetane 5, alkoxydioxetane 15, and spirocyclic dioxetane 16 under conditions of a linear temperature rise was studied, the quantum efficiency of chemiluminescence remained constant. This finding indicates that for these compounds the efficiency of excited singlet formation is temperature independent.



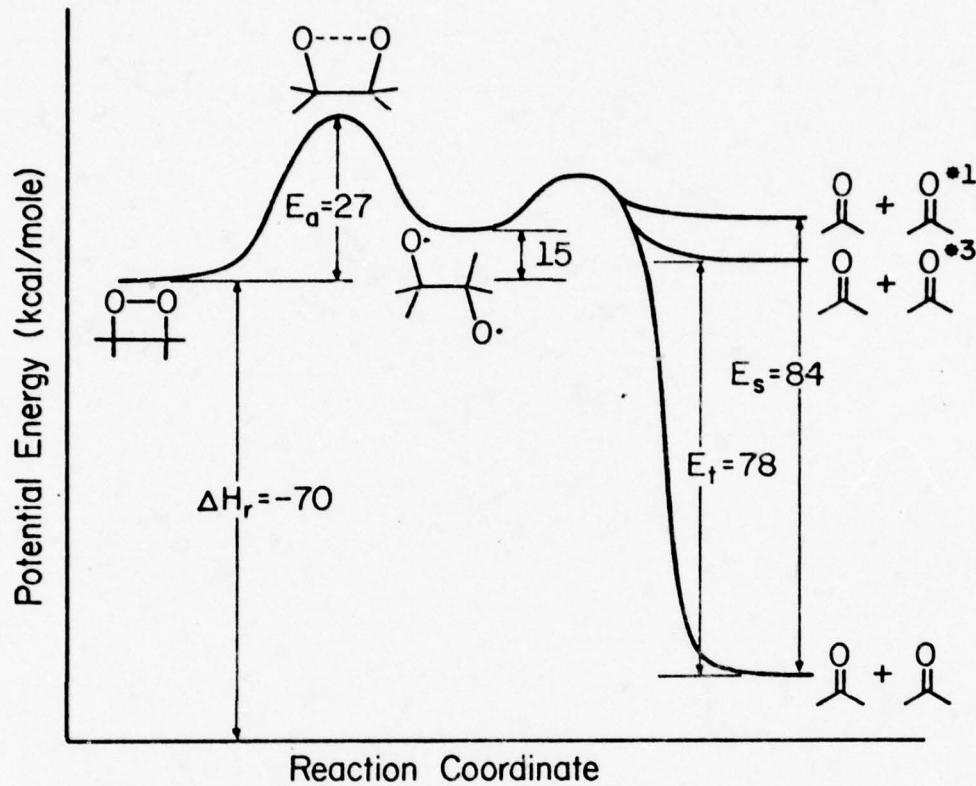
The numerous investigations of simple alkyl substituted dioxetanes during the past ten years have failed to turn up any evidence that demands a concerted fragmentation pathway. Similarly, the evidence for a biradical intermediate, or an intermediate of any kind, on the reaction path is totally circumstantial. Nevertheless, in the light of the large amount of data consistent with the stepwise path, it appears that this pathway is the best description of the thermal reactions available for simple alkyl and alkoxy substituted dioxetanes.

Over the years there have been a number of theoretical calculations on the thermolysis of dioxetanes. These have been performed on unsubstituted dioxetane which probably models simple alkyl substituted dioxetanes rather well. The earliest theoretical considerations were published by McCapra^{11a} and Kearns.^{11b} They concluded that a thermal retro 2+2 cycloaddition reaction, if it is concerted, should generate an electronically excited state of the product carbonyl compound. Several semiempirical calculations have been carried out.²⁹ The results have depended on the details of the procedure used.³⁰ Recently, Harding and Goddard¹⁸ have published the results of their *ab initio* GVB calculation for the ring opening of dioxetane. They conclude that the lowest energy path for this reaction passes through a biradical intermediate located about 14 kcal/mol above the ground state energy of dioxetane. Furthermore, they suggest that the eight states (singlet and triplet $4\pi, 2\sigma$; $3\pi, 3\sigma$; $2\pi, 4\sigma$) are separated by only ca. 3 kcal/mol. Thus the spin multiplicity of the product carbonyl compounds is predicted to depend upon the location of the excited states relative to the biradical intermediate. This prediction was experimentally demonstrated by the study of the acetyl dioxetane 10 in which the multiplicity of the methylglyoxal excited states produced approached the statistical limit of three (see above). Combination of the theoretical results of Goddard with experimentally derived parameters permits a fairly detailed sketch of the reaction coordinate for thermolysis of tetramethyldioxetane by the biradical path. This is shown in Scheme 2.

The chemistry of dioxetanes substituted with easily oxidized groups is remarkably different from that of simple alkyl substituted dioxetanes. Originally this difference was attributed to some feature of the excited state of the carbonyl compounds produced. However, the recent discovery of chemically initiated electron exchange luminescence (CIEL) by Koo and Schuster³¹ has clarified the interpretation of the data for these compounds.

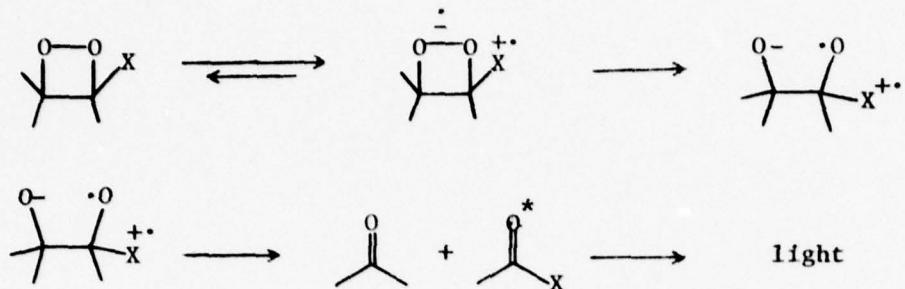
The key feature of the CIEL mechanism as it applies to dioxetanes is an electron transfer from a non-conjugated substituent to

Scheme 2



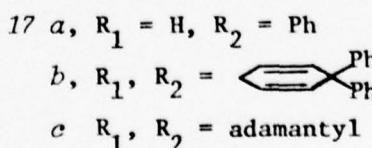
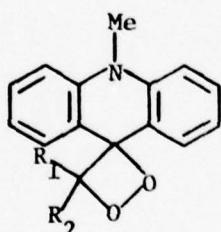
the LUMO of the dioxetane ring. The LUMO of this system is anti-bonding between the oxygen atoms.⁸ Thus, the O-O bond cleaves rapidly after the electron is transferred. Cleavage of this charge polarized intermediate to form carbonyl compounds results in the direct generation of a charge transfer resonance structural form of the excited state. The process is outlined in Scheme 3. The experimental evidence demonstrating the existence of this path for dioxetanes is presently circumstantial. Nevertheless, the weight of the evidence is quite convincing in light of the analogy to more well established systems.

Scheme 3



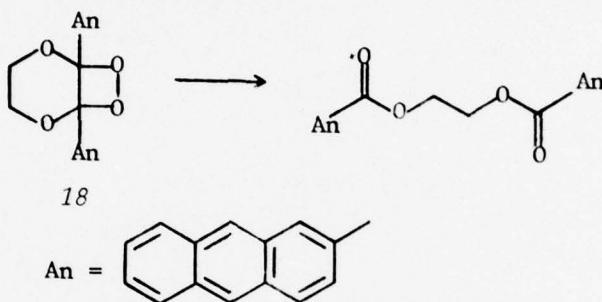
X = easily oxidized substituent

In a recent note McCapra³² described the chemiluminescence from the N-methyldihydroacridan substituted dioxetanes 17a,b,c. Several observations are of critical importance for the understanding of this system. First, these dioxetanes are somewhat less stable than their alkyl substituted counterparts. For example, 17a has a measured E_a of 19.7 kcal/mol. This observation indicates the introduction of a second path for the fragmentation reaction, one of lower energy. Second, the yield of singlet excited state products from thermolysis of these dioxetanes is unusually high. For example, the yield of excited singlet N-methylacridone from thermolysis of 17a in toluene is reported to be 25%, more than one hundred times greater than the singlet excited acetone yield from tetramethyldioxetane. These findings are consistent with the suggested intramolecular CIEEL process outlined in Scheme 3. In contrast to the results of Zimmerman and coworkers²⁴ on related systems, study of dioxetane 17b



demonstrated that there is no preferential formation of $n\pi^*$ excited states from dioxetanes with easily oxidized substituents, since there was no diminution in the yield of N-methylacridone excited singlet with this substituent.

Schaap and coworkers³³ have discovered that silica gel not only is a powerful catalyst for the decomposition of the dianthryl-substituted 1,2-dioxetane 18, but also increases the yield of excited singlet product to 12% from 0.2% for the uncatalyzed reaction. Critically, Schaap points out that only other surfaces with acidic sites are effective in catalyzing chemiluminescent cleavage of dioxetane 18. These findings can be neatly rationalized with the

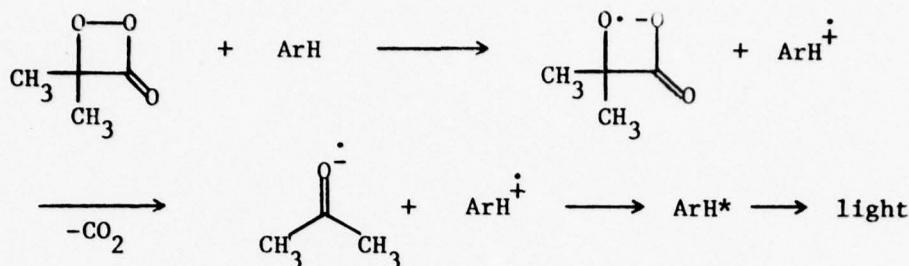


realization that the protonated peroxide is much more easily reduced than the unprotonated form. Thus, once the dioxetane is adsorbed at an acidic site on the silica gel, the anthryl substituent may be capable of donating an electron and initiating the intramolecular CIEEL process. This is analogous to the pathway outlined in Scheme 3.

Finally, Schmidt and Schuster³⁴ and Adam and coworkers³⁵ have found that alkyl substituted dioxetanones generate light in the presence of aromatic hydrocarbons mainly as a result of an intermolecular CIEEL path. It was found that the efficiency of light generation from dimethyldioxetanone is dependent on the one electron oxidation potential of an added fluorescent electron donor. This finding provides direct experimental verification of the CIEEL process for this system.

The rate and hence the efficiency for CIEEL depends upon the ease of reduction of the peroxide. Thus for diacyl peroxides which

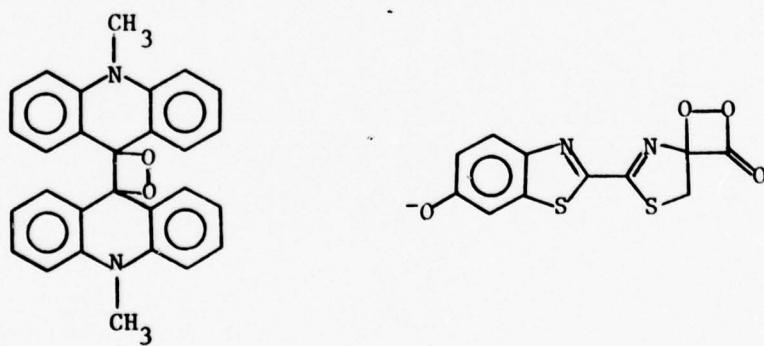
Scheme 4



are flanked by two electron withdrawing carbonyl groups, the rate of the CIEEL reaction is faster than for dioxetanones which have only one neighboring carbonyl group. Dioxetanes are relatively difficult to reduce. As a result only intramolecular CIEEL has thus far been observed and this only when the electron donor is very easily oxidized or when the dioxetane is activated by protonation.

The realization that CIEEL can generate high singlet yields and speed up the reaction of dioxetanes explains the interesting results of Singer and coworkers.³⁶ They observed that dioxetane 19, prepared by photooxygenation of 10,10'-dimethyl-9,9'-biacridylidene, decomposed to the acridone with an activation energy of only 17.2 kcal/mol and a relatively high yield of excited singlet states.

Schuster and coworkers³⁷ have applied the CIEEL mechanism to the bioluminescence of the firefly luciferin dioxetanone 20. This proposal may explain the remarkably high singlet yield from this system and the effects of structural variation on this substrate.



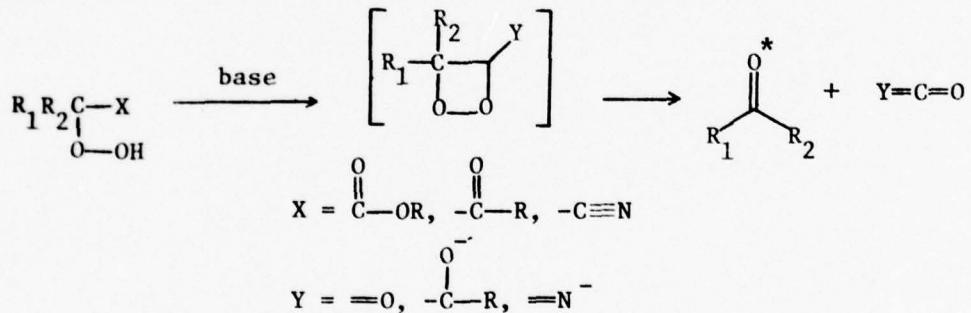
In summary, it is probably safe to point out that the last word on the mechanism of chemiluminescence from dioxetanes has not been written. The implication that the CIEEL process is operating opens up many new avenues for the preparation of highly effective and interesting light producing systems.

Light Generation Reactions Thought to Proceed Through 1,2-Dioxetanes

Before dioxetanes were isolated they were postulated to exist in a number of the reactions of hydroperoxides and in the reactions of oxygen with various organic compounds. The thermal instability of the 1,2-dioxetane ring continues to render unisolable many presumed dioxetanes. In this section we will review the recent literature of this group of compounds.

Sawaki and Ogata have reported on the chemiluminescence and kinetics for the base catalyzed reactions of α -hydroperoxy esters,³⁸ ketones,³⁹ and nitriles,⁴⁰ Scheme 5. In all cases chemiluminescence was observed when the reaction was carried out in the presence of a suitable fluorescer. The chemiluminescence efficiency,

Scheme 5

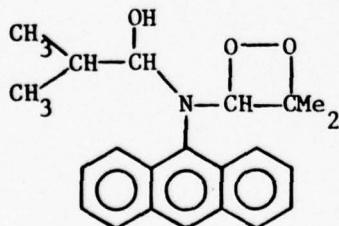


however, is generally quite low, with quantum yields in the range from 10^{-6} to 10^{-4} depending on the particular case. The kinetic studies indicate that the reaction path is complicated. For example, in the case of the hydroperoxy ketones there is a non-chemiluminescent acyclic path leading to the formation of esters in competition with cyclization to the presumed dioxetane intermediate. These competitive reactions presumably account in large part for

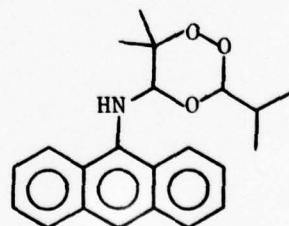
the inefficiency of light generation. Interestingly, the reactions of the α -hydroperoxy esters showed a dependence of the light yield on the nature of the fluorescer similar to that demonstrated for dimethyldioxetanone. This observation may confirm the involvement of a dioxetane intermediate in this system.

In a related study Kamiya and Sugimoto⁴¹ report that many simple ketones with abstractable α -hydrogens exhibit chemiluminescence when combined with base and oxygen in a polar aprotic solvent in the presence of dibromo- or diphenylanthracene. The authors suggest that the reaction proceeds through the α -hydroperoxy ketone to the dioxetane and thence the excited triplet carbonyl compound. The yield of excited states from these reactions ranges from 10^{-3} to 10^{-1} per cent, indicating perhaps the operation of competing reaction paths.

A report⁴² that reaction of 9-aminoanthracene with isobutyraldehyde in the presence of atmospheric oxygen gives amino dioxetane 21 has been shown to be incorrect. The compound obtained by this reaction was shown by Goto and Nakamura⁴³ to be the *as*-trioxane 22. Interestingly, this trioxane reacts with base to generate the suspected dioxetane by the route shown in Scheme 6 to generate light. This process was verified by McCapra⁴⁴ using an isotope labeling technique. Significantly, the yield of singlet excited state product from the base catalyzed reaction of 22 is reported to be 13%. This high singlet state yield and the instability of the dioxetane suggests that the major excitation process may be an intramolecular CIEEL path.

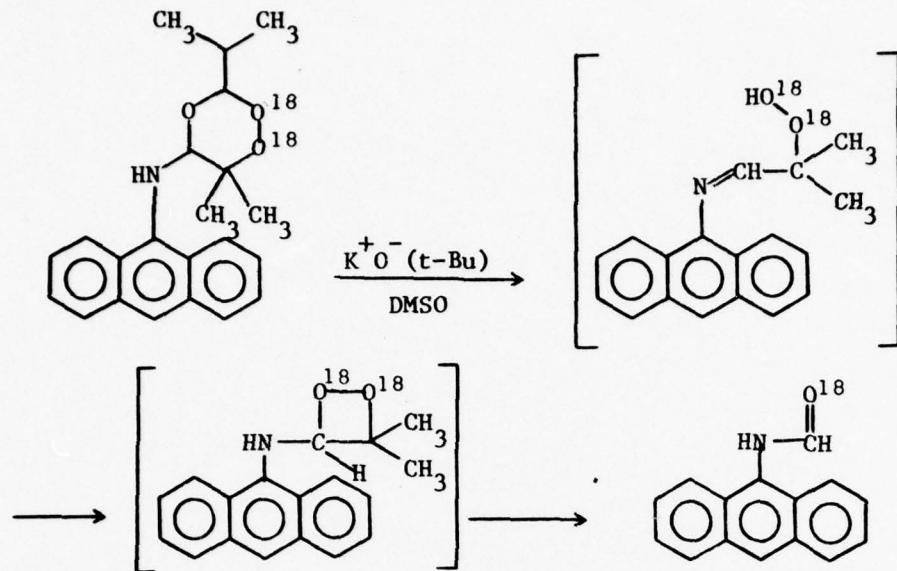


21



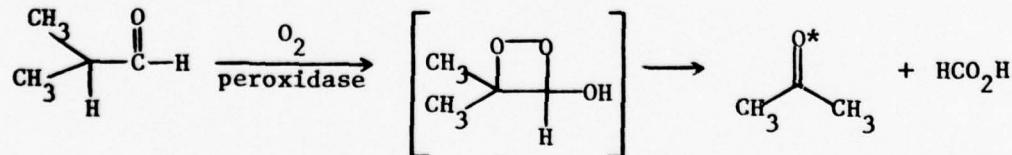
22

Scheme 6



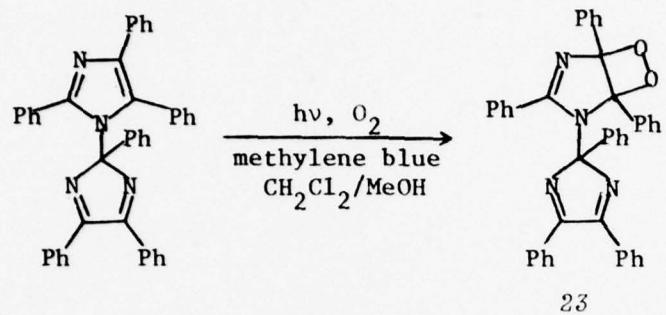
A finding of potential importance was reported by Cilento and coworkers.⁴⁵ They found that the oxidation of isobutyraldehyde in the horseradish peroxidase-O₂ system produces detectable quantities of acetone triplet. The mechanism for this enzyme initiated chemiluminescent reaction is outlined in Scheme 7. The intermediacy of a dioxetane in this process may foreshadow the involvement of electronically excited state products in many enzymatic oxidation reactions. Along these same lines, Cilento and coworkers⁴⁶ report that certain oxidizable auxin derivatives are chemiluminescent under conditions that mimic the *in vivo* chemiluminescence of known luciferins.

Scheme 7



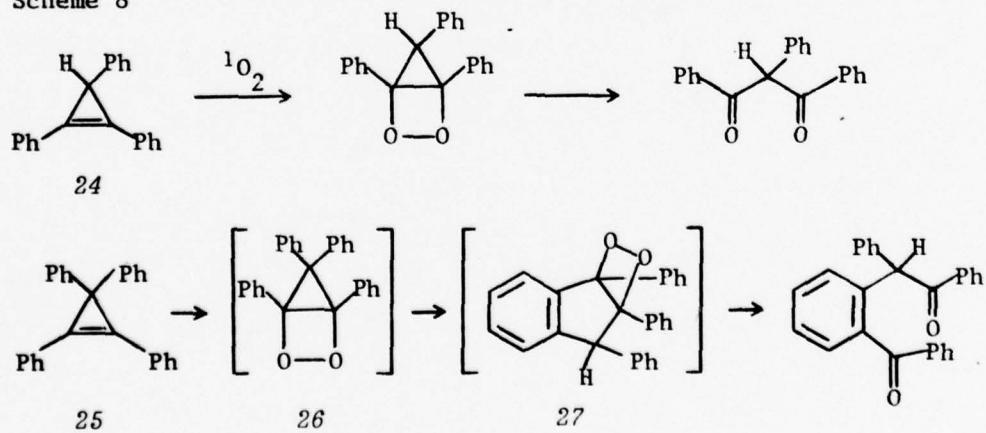
Rio and Serkiz⁴⁷ report that photooxidation of the dimer of 2,4,5-triphenylimidazoyl radical in polar solvent leads to the gen-

eration of the heterobicyclic dioxetane 23. However, the isolated peroxide exhibits stability unexpected for a compound of this structure (mp 117°). Further consideration of this interesting compound must await further proof of its structure.



Griffin, Turro and coworkers⁴⁸ have probed the photooxidation of tri- and tetraphenylcyclopropenes. Interestingly, these authors report a remarkable sensitivity of the reaction to the substituents. Comparison of the photooxidation of cyclopropenes 24 and 25 revealed different reaction paths, Scheme 8. The dioxetanes were implicated in this process on the basis of observed chemiluminescence. The authors point out that the rearrangement of the initially formed dioxetane 26 to dioxetane 27 may not in fact occur. Dioxetane 27 could be a result of rearrangement of the intermediate perepoxide resulting from polar addition of oxygen to cyclopropene 25.

Scheme 8



Formation and Reaction of Dioxetanes in the Gas Phase

Most of the chemistry of dioxetanes that has been investigated has been carried out in solution. Reaction in the gas phase provides the opportunity to study chemical activation phenomena and to obtain high resolution emission spectra. In this section we will briefly review the recent work in this area of dioxetane chemistry.

The reaction of 1O_2 with ethyl vinyl ether in a discharge flow system at 620°K was investigated by Bogan and coworkers.⁴⁹ They observed chemiluminescence which was attributed to emission from electronically excited formaldehyde. The activation energy for production of the chemiluminescence was found to be 9.8 kcal/mol. The rate limiting step in the reaction sequence leading to chemiluminescence was assigned to the addition of 1O_2 to the olefin and thus the activation energy refers to this process. Experiments showed that the lifetime of the dioxetane under these conditions was less than 10^{-7} sec. These results, in combination with thermochemical calculations, were interpreted to indicate that the dioxetane was formed at an energy more than 45 kcal/mol above ground state dioxetane and that this highly excited intermediate rapidly cleaved to produce vibrationally and electronically excited carbonyl group fragments. A study employing ethylene as a reactant gave similar results.⁵⁰

In a study of a wide variety of olefins capable of forming formaldehyde upon reaction with 1O_2 in the gas phase, Bogan and co-workers⁵¹ uncovered the interesting result that the intensities of vibronic hot bands in the formaldehyde emission spectrum was dependent on the nature of the olefin used. It was found that the hot band intensity is directly related to the available energy and inversely related to the number of vibrational modes of the dioxetane.

In a different type of gas phase study Haas and Yahav⁵² irradiated tetramethyldioxetane with a TEA CO₂ laser. They obtained time-resolved spectra of the chemiluminescence following absorption of the ir pulse. Their studies showed that the excited dioxetane decomposed by at least two pathways, a unimolecular collision-free route and a collision-induced mechanism. These authors suggest that

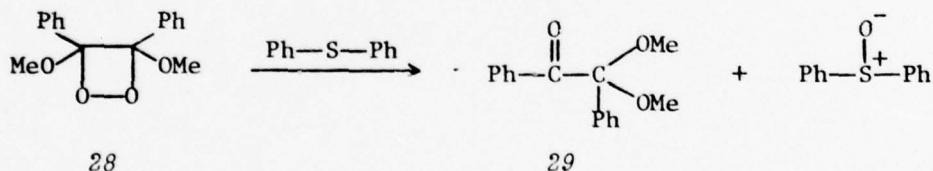
the chemiluminescence observed may be due to direct formation of an acetone excimer. Such an excimer does not exist in solution.⁵³

In a similar study Flynn and coworkers⁵⁴ irradiated tetramethyldioxetane in a methylfluoride bath. In this case the energy is absorbed initially by methyl fluoride and subsequently transferred to the dioxetane. The experiments showed that the reaction is initiated by ir light absorption by CH₃F which leads to generation of acetone fluorescence. The mechanism for the energy transfer was assigned to thermal heating of the reaction vessel by the laser pulse (temperature-jump).

Non-Chemiluminescent Reactions of Dioxetanes

Investigations of 1,2-dioxetanes have mainly centered on the reactions that lead to excited state generation. However, there has developed a body of knowledge concerning the strictly ground state chemistry of this ring system. In this section we will review the recent advances in this area.

Wasserman and Saito⁵⁵ report that thermolysis of dimethoxydiphenyldioxetane (28) results as expected in a quantitative yield of methylbenzoate. However, reaction of this dioxetane with diphenyl sulfide in ether-methanol gave benzil dimethylketal (29) and diphenyl sulfoxide. These authors suggest that this reaction proceeds

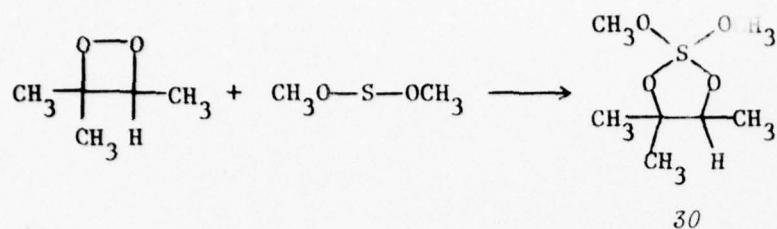


28

29

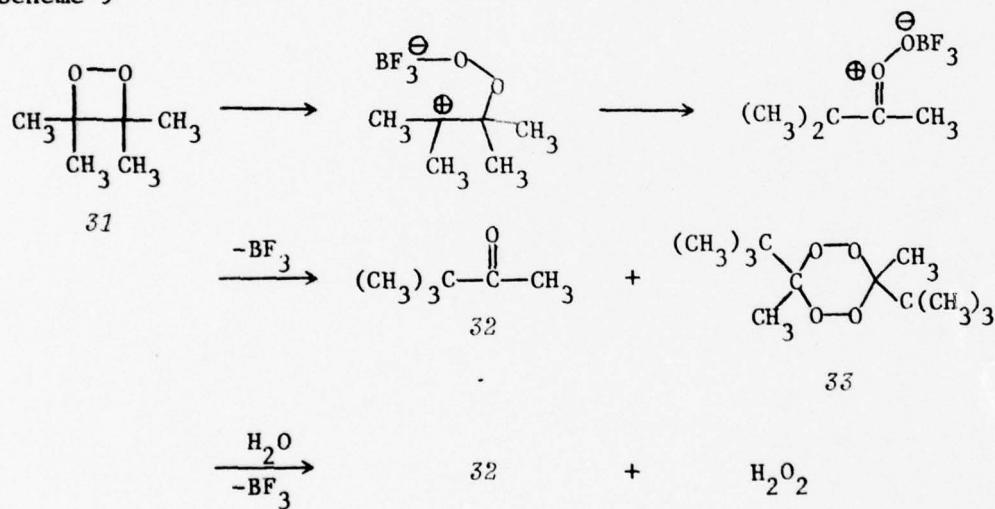
through a zwitterionic intermediate. Denny and coworkers⁵⁶ investigated the related reaction of dioxetanes with alkyl sulfoxylates. In this case, reaction of trimethyldioxetane with dimethylsulfoxylate in methylene chloride at -78° led to the formation of sulfurane 30. The sulfuranes, however, could not be isolated. This transformation is reminiscent of the formation of isolable phosphoranes from dioxetanes and trialkylphosphites reported by Bartlett and

coworkers.⁵⁷



The rearrangement of tetramethyldioxetane (31) catalyzed by boron trifluoride in aprotic solvents was studied by Bartlett and coworkers.⁵⁸ They report that treatment of the dioxetane with BF_3 in methylene chloride at -78° for 30 min followed by a methanol quench led to formation of pinacolone (32), cyclic pinacolane di-peroxide (33), acetone, and hydrogen peroxide (Scheme 9). This reaction represents the only example of the catalysis of a dioxetane reaction that is not dominated by a retro 2+2 cycloaddition.

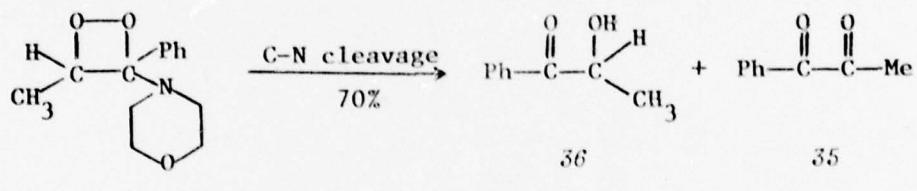
Scheme 9



The rapid reaction of dioxetanes with transition metals has plagued the study of the chemiluminescence of these compounds. Bartlett and McKennis⁵⁹ have studied the reaction of tetramethyldioxetane with a number of iridium and rhodium complexes that are known to undergo oxidative additions. This study complements their earlier work in which it was found that for a series of divalent

metals the catalytic rate paralleled the Lewis acidity.⁶⁰ In this case, it was found that the rhodium catalysts act by oxidative addition to cause a net dark decomposition of tetramethyldioxetane. Attempts to fit the result to a Hammett linear free energy relationship were only partially successful.

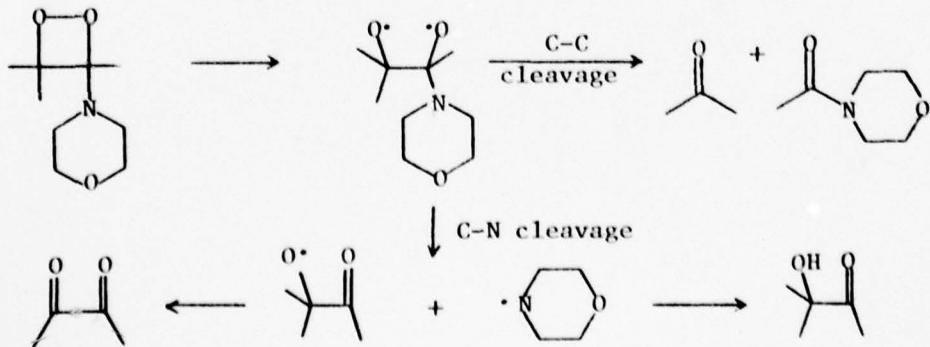
There are a number of unimolecular rearrangements of appropriately substituted dioxetanes that do not involve cleavage of the central carbon-carbon bond of the ring. Ando and coworkers⁶¹ have studied the thermal cleavage of some unisolated amino substituted dioxetanes and report that in certain circumstances the chemistry is dominated by carbon-nitrogen bond cleavage. Thus, dioxetane 34 prepared by photooxidation of the corresponding enamine spontaneously decomposes at room temperature to form diketone 35 and hydroxyketone 36 as well as morpholine and substituted morpholine.



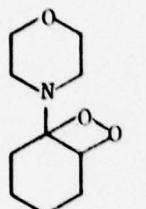
34

The mechanism suggested for this intriguing reaction is shown in Scheme 10. Unfortunately, there is no indication in the report about the occurrence of chemiluminescence as a result of this reaction.

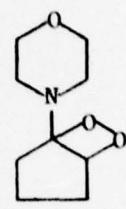
Scheme 10



Wasserman and Terao⁶² have prepared and isolated at low temperature amino substituted dioxetanes 37 and 38 from the photooxygenation of the corresponding olefins. Thermolysis of these dioxetanes leads primarily to diketones, evidently by a β -elimination pathway, Scheme 11.

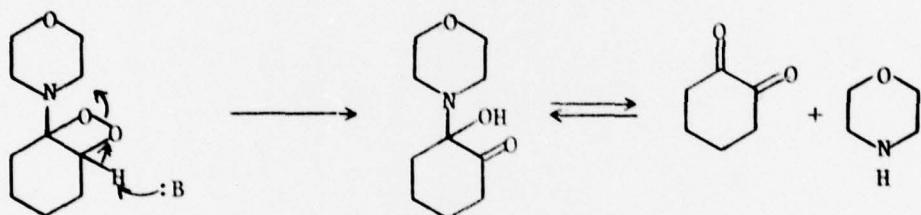


37



38

Scheme 11



Dioxetanes as a Tool

Apart from the interest in the chemiluminescence of dioxetanes *per se*, there has been considerable success in the application of dioxetane generated excited states to the study of other chemical phenomena. These systems can be considered extensions of the concept advanced by Emil White as photochemistry without light.⁶³ The major advantage of dioxetane generated over photochemically generated excited states is specificity. The chemical generation overcomes the problems of competitive absorption and insures the initial location of the excitation energy.

These techniques were employed by Adam and coworkers⁶⁴ to determine the rate constant for singlet-singlet energy transfer from dioxetane generated singlet acetone to ergostatetraenone. At 51° in acidified acetonitrile this rate constant is reported to be ca.

$10^{12} \text{ M}^{-1} \text{s}^{-1}$.

In a related study Schmidt, Kelm, and Brauer⁶⁵ used external pressure to probe the mechanism for the net triplet to singlet energy transfer from triplet acetone to 9,10-dibromoanthracene. The triplet acetone was generated by thermolysis of tetramethyldioxetane. This study showed that the mechanism of this energy transfer probably proceeds by an initial exchange triplet-triplet interaction to generate an upper triplet of the anthracene. Exothermic triplet to singlet intersystem crossing aided by the heavy atoms then generates the observed emitting singlet.

Conclusion

In this review we have summarized the results of many recent investigations of the chemistry of the 1,2-dioxetane ring system. The multifaceted reactions of these compounds have provided much information about the reactivity of strained peroxides and high energy content molecules in general. The investigations of the past three years have served to both clarify and enlarge the entire spectrum of known chemical reactions. Our prejudice causes us to focus attention on the chemiluminescent aspects of these molecules. Many experiments have been done to elucidate the detailed chemical steps responsible for excited state generation. Mechanisms have been proposed that cleanly account for much of the known experimental evidence. The future holds critical chemical and spectroscopic tests of these reaction schemes.

Acknowledgment

This work was supported in part by the Office of Naval Research, the Petroleum Research Fund administered by the American Chemical Society, and the Research Corporation. G.B.S. is a fellow of the Alfred P. Sloan Foundation.

Table 1

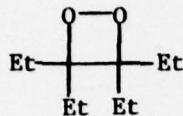
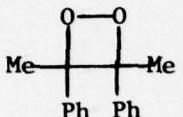
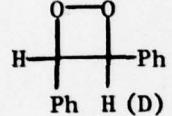
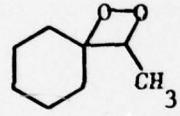
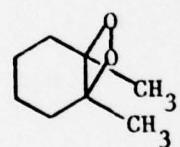
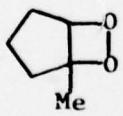
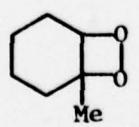
Structure ^a	Method of Prep. ^b	E _a	ϕ_x^c	Ref
	Elim	31.0 ± 1	0.5	26
	Elim	25 ± 1	0.30	66
	Elim	22.3 ± 1.9	0.10	14
	Elim	--	--	3b
	Elim	25.7 ± 0.7	--	3b
	Elim	25.2 ± 0.5	0.1	67
	Elim	23.7 ± 0.5	0.8	67

Table 1 (continued)

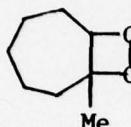
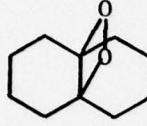
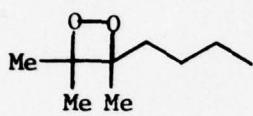
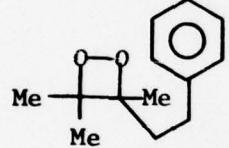
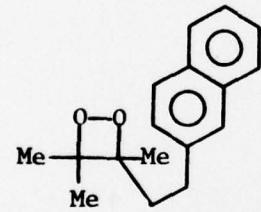
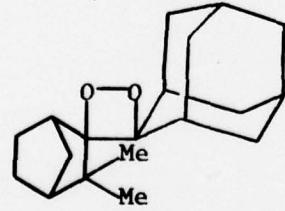
Structure ^a	Method of Prep. ^b	E _a	ϕ _x ^c	Ref
	Elim	25.9 ± 0.5	0.3	67
	Elim	22.7 ± 0.9	--	3b
	Elim	25.3 ± 0.5	0.48	67
	Elim	25.5 ± 0.5	0.45	67
	Elim	25.7 ± 0.5	0.46	67
	¹ O ₂	30.3 ± 1.3	--	68

Table 1 (continued)

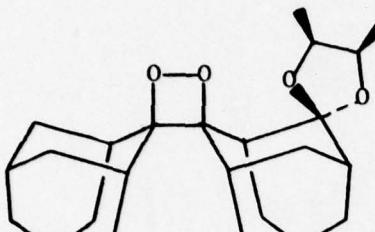
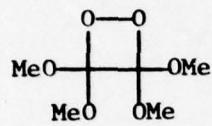
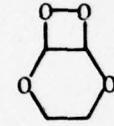
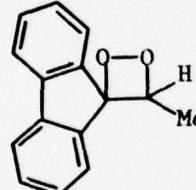
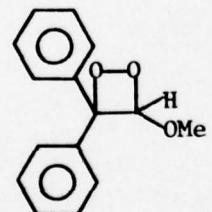
Structure ^a	Method of Prep. ^b	E _a	ϕ _x ^c	Ref
	¹ O ₂	--	--	69
	¹ O ₂	28.6 ± 1	0.1	15
	¹ O ₂	24.6 ± 1	0.3	15
	Elim	21.0 ± 1	--	70
	Elim	26.1 ± 1	--	70

Table 1 (continued)

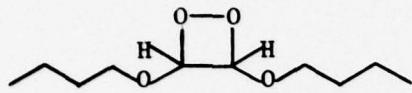
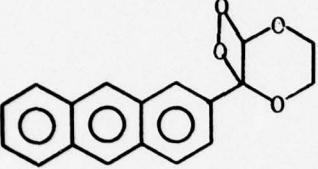
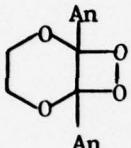
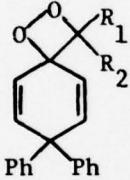
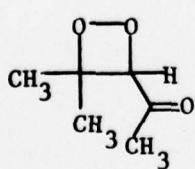
Structure ^a	Method of Prep. ^b	E _a	ϕ_x^c	Ref
	${}^1\text{O}_2$			28
	${}^1\text{O}_2^d$	--	--	5
	${}^1\text{O}_2$	--	0.12 ^e	33
An = 2-Anthryl				
				
a, R ₁ = Me, R ₂ = Ph	${}^1\text{O}_2$	--	$\alpha = 0.20$	24
b, R ₁ = Me, R ₂ = m-MeOPh			$b = 0.16$	
c, R ₁ = Me, R ₂ = 2-Naph			$c = 0.14$	
d, R ₁ = Bu, R ₂ = Ph			$d = 0.17$	
e, R ₁ = R ₂ = Me			$e = 0.13$	
	Elim	26	0.17	20

Table 1 (continued)

Structure ^a	Method of Prep. ^b	E _a	ϕ_x^c	Ref
	$^{10}_2$	f	--	71
	$^{10}_2$	f	--	62
	$^{10}_2$	19.7	0.25	32
	$^{10}_2$	26.3	0.12	32
	?	--	0.059	32

Table 1 (continued)

Structure ^a	Method of Prep. ^b	E _a	ϕ _x ^c	Ref
	¹ O ₂	17.2 ± 0.3	0.076	36
	¹ O ₂	--(mp 117°)--		47
	¹ O ₂	--	--	28,72

^aOnly those dioxetanes which have been isolated and characterized during the period covered in this review are included in this table.

^bElim indicates that the dioxetane was prepared by the eliminative cyclization of the appropriate β-substituted hydroperoxide, ¹O₂ indicates that the dioxetane was prepared by reaction of the corresponding olefin with singlet oxygen.

^cQuantum yield of electronically excited states that are formed during thermolysis of the dioxetane.

^dPrepared by silica gel catalyzed rearrangement of the endoperoxide.

^eCatalyzed by silica gel, the singlet yield is 0.002 for the uncatalyzed reaction.

^fUnstable at room temperature and only partially characterized.

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